

## Soft Modes at the Stacking Faults in SiC Crystals

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We use first-principles calculations based on density functional theory to determine and understand the driving force of the observed stacking fault expansion in SiC. We verify the suggestion based on recent experiments that the free energy difference between the faulted and the perfect structures is responsible for this expansion, and show that its origin lies in a large entropy associated with soft vibrational modes of the faulted SiC structure. These soft modes involve shearing of SiC on a long length-scale and are absent in related group IV semiconductors, such as Si, Ge and C.

Among the group IV semiconductors (Si, Ge, C, SiC), SiC is unique in exhibiting hundreds of polytypes that differ only in the stacking sequence of Si-C double layers<sup>1</sup>. Due to its excellent physical properties such as high hardness, low density and thermal expansion, it has found numerous applications in automotive components, seal faces, armour, mechanical seals, bearings, heat exchanger tubes, etc.<sup>2</sup> As it is available in large single crystal wafer form<sup>3</sup>, SiC is also interesting as a wide band-gap semiconductor for electronic applications: it is a promising material for the next generation power diodes owing to its low on-resistance, high break-down voltage, radiation stability and low switching losses<sup>4</sup>. Recently, there have been efforts aimed at developing dilute magnetic semiconductors (DMS)<sup>5</sup> based on SiC for use in spintronic devices.

However, formation of line defects<sup>6,7</sup> and expansion of stacking faults<sup>8</sup> in SiC crystals are known to be possible causes of degradation of the performance of SiC-based power diodes. Understanding the mechanism of stacking fault expansion in SiC is important to its use in electronic devices and it may also shed light on a related fundamental question of the stability of polytypes of SiC<sup>9</sup>. It is also interesting to find out if this mechanism operates in other group IV semiconductors.

In a power electronic device current densities as high as 50-100 A/cm<sup>2</sup> lead to an enormous amount of heating and operational temperatures are higher than the normal ones. Optical emission microscopy (OEM) based experiments on 4H-SiC used in high current density conditions revealed stacking fault expansion in the basal plane of the system, establishing that hexagonal polytypes of SiC are unstable at high temperatures with respect to formation and expansion of stacking faults<sup>8</sup>. Based on this work, free energy differences was suggested to be the driving force of stacking fault expansion.

Many groups have carried out first-principles investigation of the stability of various polytypes of SiC and their

stacking faults<sup>10,11,12</sup>. With very small energy differences involved, the exact ordering energies of polytypes is a bit scattered in these studies. However, they all estimated very small but positive stacking fault energies. It is not clear yet what drives the stacking fault expansion in SiC at finite temperature.

In this work, we use first-principles calculations to determine free energy differences between different polytypes and stacking-faulted structures of SiC through determination of configurational and vibrational entropies. Configurational and vibrational contributions to free energy are determined from the knowledge of full stacking fault energy surface<sup>13</sup> and of the vibrational spectrum respectively. We show that soft shear modes developed in the faulted structures drive their stability at finite temperature.

Diamond (or zincblend, labeled here as 3C) structure, the common polytype of all group IV semiconductors, can be described as two interpenetrating FCC lattices separated by  $[111]a/4$ ,  $a$  being the lattice constant. Along  $[111]$  direction, triangular lattices of atoms described with high symmetry positions A, B and C are stacked periodically as (AaBbCc), where upper and lower case letters label the two FCC sublattices. In case of SiC, carbon atoms occupy sites of the second sublattice. Atoms in the polytypes obtained with a variation in this stacking sequence (studied in this work) are all tetrahedrally coordinated. In the Hagg notation<sup>14</sup> used commonly in the representation of stacking sequences, (AaBb), (BbCc) and (CcAa) are denoted as (+), and the anti-cyclic stacking sequences eg. (BbAa) are denoted as (−). Thus, 3C-SiC (with AaBbCc stacking), 4H-SiC (with AaBbAaCc stacking) and 6H-SiC (with AaBbCcAaCcBb stacking) polytypes are represented with periodic units of (+++), (++−) and (+++−−), respectively. In the Hagg notation, a stacking fault is introduced simply through a change in sign. Deformation type stacking faults in 3C-SiC, 4H-SiC and 6H-SiC systems, which are bordered by Shockley partials on the basal plane, are (...+++|−++++...), (...++−|−+−−+−−...) and (...+++−−−|−+−−−+−−−...), respectively, where the symbol ‘|’ indicates the stacking fault

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plane(10). There are two types of (111)/(0001) planes where a deformation type stacking fault can form: (a)  $A|a$  called as “shuffle”, and (b)  $a|B$  called as “glide”.

Our calculations are based on first-principles pseudopotentials within Density Functional Theory as implemented in the Plane Wave Self Consistent Field (PWSCF)<sup>15</sup> code. We employ a local density approximation (LDA) to exchange correlation energy functional and use ultra-soft pseudopotentials<sup>16</sup> to represent interaction between ionic cores and valence electrons, and a plane wave basis with an energy cut off of 30 Ry (180 Ry) in the representation of the Kohn-Sham wavefunctions (density). Supercells with 12 atomic planes for elemental semiconductors and 24 atomic planes for SiC are used in the calculations of configurations with of stacking faults. Corresponding Brillouin zones are rather small in the  $z$ -direction (perpendicular to the plane of the fault) and integrals over them were sampled with a uniform  $5 \times 5 \times 1$  mesh. Positions of atoms inside the supercell were relaxed to attain a minimum energy structure using Hellman-Feynman forces in the Broyden, Fletcher, Goldfarb, Shanno (BFGS)-based method<sup>17</sup>. Structural parameters for Si, Ge and C in diamond structure and 3C, 4H and 6H polytypes of SiC agree with the experimental values within the typical LDA errors. We find the cohesive energies of all the SiC polytypes are rather close to each other and both 6H and 4H structures are almost equal within the calculational errors and the lowest in energy.

We first determined generalized stacking fault energy ( $\gamma$ -) surfaces<sup>13</sup> for the (111) or basal planes of all the crystals studied here. It corresponds to the energy required to displace a half of the crystal on one side of the given plane relative to the other and exhibits periodicity of the crystal plane. For a given displacement path going from the origin to a burgers vector  $\mathbf{b}$ , a maximum in the  $\gamma$ -surface gives the the energy barrier for slip along that path. The lowest of these barriers among the family of various paths joining origin and  $\mathbf{b}$  is called the unstable stacking fault energy<sup>18</sup>  $\gamma_{us}$ . A local minimum of the  $\gamma$ -surface defines an intrinsic ( also called deformation(10) ) stacking fault. We used fourier transform to analyze the  $\gamma$ -surface by sampling it on a uniform  $5 \times 5$  mesh in the planar unit cell.

In all the tetrahedral systems considered here, our results rule out the possible slip on shuffle plane as it is energetically 25-36 times more expensive than the slip on the glide plane. The  $\gamma$ -surfaces of the glide plane of all tetrahedral semiconductors are topologically similar (see Fig. 1 for the  $\gamma$ -surface of SiC). We find  $\gamma_{us}$  is about the same for the three polytypes of SiC, which is about half the  $\gamma_{us}$  of diamond and larger by 80 % than that of Si and Ge (see Table I). The trend in our estimates of  $\gamma_{us}$  suggests that nucleation of dislocations on (111) planes is much easier in Si and Ge than in SiC and diamond<sup>18</sup>. The energy of intrinsic stacking fault located at  $(2/3, 1/3)$  in the  $\gamma$ -surface ( $\gamma_{isf}$ ), bears a rather different trend: it is smallest for the polytypes of SiC and

TABLE I: Calculated and experimental estimates of intrinsic ( $\gamma_{isf}$ ) and unstable ( $\gamma_{us}$ ) stacking fault energies for the slip in glide plane.

System	$\gamma_{isf}$ (calc.) (mJ/m <sup>2</sup> )	$\gamma_{isf}$ (expt.) (mJ/m <sup>2</sup> )	$\gamma_{us}$ (J/m <sup>2</sup> )
Si	46.9	69 <sup>27,28</sup>	1.7
C	250	279 <sup>28,29</sup>	5.5
Ge	48.5	—	1.6
3C-SiC	10.1	—	2.8
4H-SiC	9.1	14.7 $\pm$ 2.5 <sup>11</sup>	2.9
6H-SiC	2.6	2.5 $\pm$ 0.9 <sup>12</sup>	2.9

5 times larger for Si and even larger for diamond. These values generally agree well with experimental estimates and other calculations<sup>19</sup> wherever available. Significantly lower values of  $\gamma_{isf}$  (and somewhat large  $\gamma_{us}$ ) of SiC support large areas of stacking faults which sometimes extend right upto the crystal boundaries with partials disappearing at the surface.

We estimated the free energies of perfect and faulted SiC with  $F = E + F_{config} + F_{vib}$ , where  $E$  is the total energy obtained with DFT calculations,  $F_{config}$  and  $F_{vib}$  are the configurational and vibrational contributions to free energy respectively.  $F_{config}$  is obtained from the de-

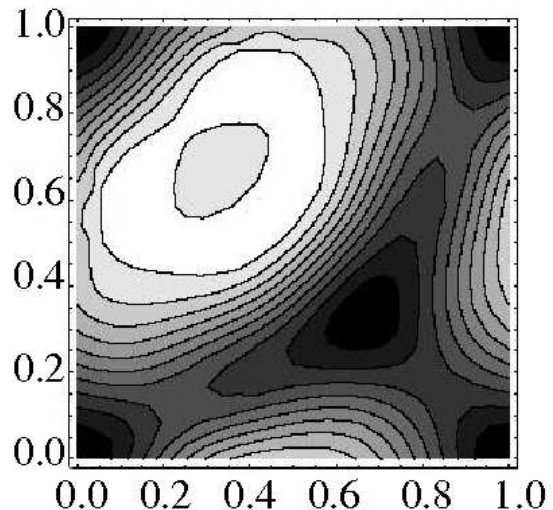


FIG. 1: Contour plot of Generalized Stacking Fault Energy( $\gamma$ ) Surface for slip on the glide plane of 4H-SiC

tailed structure of basins of the  $\gamma$ -surface centered at  $(0,0)$  and  $(2/3, 1/3)$  corresponding to perfect and faulted structures. We approximated the  $\gamma$ -surface in the neighbourhood of the centres  $(x_0, y_0)$  of these basins (sampled by the system at finite temperature  $T$ ) with a symmetry invariant parabolic form:  $E(x, y) = E_o + K((x - x_o)^2 + (y - y_o)^2)$ , to determine configurational contribution to

free energy<sup>20</sup>

$$F_{conf} = -k_B T \text{Log}\left(\frac{K}{2\pi k_B T}\right) \quad (1)$$

where  $x$  and  $y$  are the components of displacements for which the GSF has been obtained, the parameter  $K$  was determined from DFT calculations carried out on a fine uniform  $3 \times 3$  mesh over an area of  $0.174 \text{ bohr}^2$  centered in each basin. Similarly, vibrational free energy is determined with

$$F_{vib} = -k_B T \sum_{iq} \text{Log}\left(2 \sinh\left(\frac{\hbar \omega_{iq}}{2k_B T}\right)\right) \quad (2)$$

$\omega_{iq}$  being the frequency of a phonon  $i$  with wave vector  $q$ , obtained with DFT linear response calculations<sup>21</sup>. We sampled  $q$  at  $\Gamma$  and  $K$  points with weights of  $\frac{1}{3}$  and  $\frac{2}{3}$  respectively, omitting acoustic modes at the  $\Gamma$ .

The stacking fault energy as a function of temperature is obtained using:  $\gamma_s(T) = \gamma_s(0) + \Delta F_{conf}(T) + \Delta F_{vib}(T)$  where  $\gamma_s(0)$  is the stacking fault energy at zero temperature, and  $\Delta F$  is the difference in free energy of the perfect and the faulted structures. In the approximation that phonon frequencies do not change with temperature, free energies vary linearly with temperature at low  $T$ . For 4H-SiC, we find the vibrational contribution to  $\Delta F/T$  ( $-0.2037 \times 10^{-3} \text{ J/m}^2 \text{ K}$ ) dominating over the configurational contribution ( $0.27 \times 10^{-5} \text{ J/m}^2 \text{ K}$ ). Evidently, vibrational entropy plays a crucial role in stabilizing the faulted 4H-SiC structure at high temperatures. The stacking fault energy as a function of temperature (see Fig. 3) reveals that the faulted structure is energetically favorable at 60 K, supporting the observed stacking fault expansion and the suggestion that it is driven by the free energy difference<sup>8</sup>.

We determine the precise microscopic mechanism that stabilizes the faulted structure by examining mode-by-mode contribution to the vibrational free energies. In comparison with the perfect 4H structure, there emerge four soft phonon modes (see Figure 2) at  $\Gamma$  point in the faulted 4H structure with frequencies 107.3, 107.4, 109.9, 110.0  $\text{cm}^{-1}$ , which lowers its free energy through its contribution to the entropy. We note that most of these soft modes involve shear straining of the structure over a longer length-scale in a direction perpendicular to the plane of the fault. These soft modes couple with shear strain and can drastically reduce shear elastic moduli which in this case is  $C_{44}$ . Thus, large shear strains can be induced even with small shear stresses in the system. We note that our estimate of the temperature above which the faults get stabilized can have large errors due to many approximations made in our analysis. However, the mechanism we have identified here is expected to be reliable. In contrast to the 4H structure, we find the configurational contribution to free energy alone is adequate in stabilizing faults in the 6H structure. This means the energy basin of the perfect 6H structure is stiffer than the energy basin of its faulted form yielding larger configurational entropy to the faulted form.

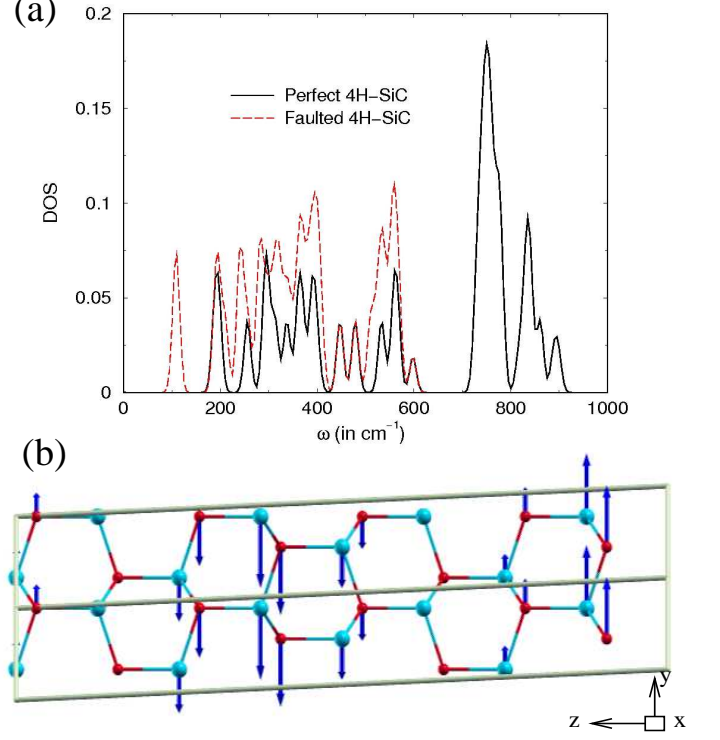


FIG. 2: (a) Phonon Density of States of perfect and faulted 4H-SiC (b) Soft shear phonon mode of frequency  $107.3 \text{ cm}^{-1}$  in faulted 4H-SiC

Finally, we would like comment on the relative stability of 4H and 6H structures of SiC. Many groups<sup>22,23,24,25</sup> have reported energies of these structures within a couple of meV per atom of each other. However, these are very small energies and we think both structures are equally stable at  $T=0 \text{ K}$  within our calculational errors. By including vibrational contribution to free energy at nonzero temperature, we find that the 6H structure is more stable than the 4H structure by a sizeable difference in free energy (with a rate of  $6 \times 10^{-5} \text{ eV/atom/K}$ ). Along with our earlier conclusion that the 6H structure would also tend to form faults at finite temperature, we conclude that both 4H and 6H structures of SiC are metastable at finite temperature.

In summary, we have verified the speculation based on experimental work<sup>8</sup> that free energy difference is the driving force of stacking fault expansion in SiC. The stability of the faults has been shown to arise from the vibrational entropy and particularly soft phonon modes that involve atomic displacements that shear the faulted structure on long length-scale. As a result, stacking faults are expected to grow at finite temperature in both 4H and 6H polytypes of SiC and this is a fundamental limitation of SiC for use in devices. Our work should stimulate further theoretical and experimental work that focus on destabilizing stacking faults in SiC through suitable doping or other means.

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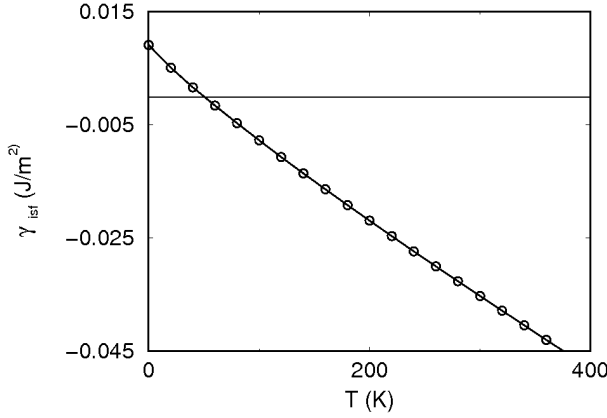


FIG. 3: Stacking Fault energy ( $\gamma_{isf}$ ) of 4H-SiC as a function of temperature

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